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THE PRESSURE-VOLUME-TEMPERATURE RELATIONS OF FIFTEEN LIQUIDS.

BY P. W. BRIDGMAN.

INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED WITH AID FROM THE RUMFORD FUND.

(Continued from page 3 of cover.)

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Introduction.

This paper contains determinations of the volume of a number of liquids between 0° and 95° C and up to 12000 kg/cm² by the sylphon method which has been applied and discussed in detail in two preceding papers.[1] The new liquids investigated here fall into three groups. The first group consists of only a single liquid, triethanolamine. The reason for investigating this was that it was hoped that its structural similarity to glycerine would throw some light on the cause of incompressibility in liquids, glycerine being the most incompressible organic liquid yet measured. The second group consists of nine alkyl halides, namely the propyl, butyl, and amyl chlorides, bromides, and iodides. Halogen compounds were chosen for investigation because previously interesting results had been found for mono-clorbenzene and mono-brombenzene as compared with simple benzene, and it seemed that the most promising method of investigating the effect of the halogen was to systematically examine a whole

series of compounds. Finally, the third group, five of the isomers of octanol, was investigated in order to find more in detail the effect of systematic structural changes.

The technique of the manipulations and the computations is almost exactly the same as before, particularly in the second of the two papers. The only significant differences are: (1) that readings of volume at atmospheric pressure were made at both 0° and 50°; this is preferable to obtaining the volume at 50° and atmospheric pressure by an extrapolation from readings between 200 and 1000 kg as was done in the previous paper: (2) in the case of the alkyl halides it was possible to make readings at 0° in most cases to 12000 without freezing, thus permitting more complete data than was possible for many of the previous liquids which freeze at lower pressures.

The liquids of the first two groups were obtained from the Eastman Kodak Co. Several of these were further purified, as will be described in the detailed presentation of data. Preliminary examination had shown that there is no important chemical action between these liquids and the solder and brass of which the sylphon is constructed.

For the octanols I am much indebted to Professor E. Emmet Reid of the Johns Hopkins University, who has prepared the complete set of the 22 isomers of octanol, and who placed at my disposal the entire set. Many of the physical properties of these isomers have already been determined. From a study of them, and in particular the densities at atmospheric pressure, I selected the five which seemed most likely to have significant differences in compressibility, and the results for these are presented here.

The freezing pressure of the isomers of octanol is much less than that of the other liquids of this paper, so that a fairly definite indication of where it is located was essential to avoid damage to the sylphon. A preliminary series of measurements was therefore made on the five isomers. The approximate freezing pressure at room temperature was determined by the method of piston displacement which I have previously applied in measuring freezings and polymorphic transitions under pressure.[2] The isomer was separated from the pressure transmitting liquid by mercury. The apparatus, which was specially constructed for these measurements, differed from that used before only in its small size, which was necessary because of the limited amount of the isomers available. Definite indications of freezing were obtained, but the freezing was never sharp, so that it did not seem worth while to try to get precise freezing curves or the change of volume on freezing. The melting temperatures at atmos-

pheric pressure had been determined by Professor Reid. This, together with the freezing pressure at room temperature gave sufficiently good indications of the pressure range to be avoided with the sylphon. In Tables XI to XV the region in which the material is solid is indicated by the blank places; these should not be used, however, to get more than very rough coordinates for the melting curves.

In addition to rough measurements of melting, other measurements were also made on the isomers of octanol at room temperature. Some question as to whether the compounds may have experienced changes between the time of formation and the time of the compressibility measurements arose because of discrepancies between the densities provided me by Professor Reid and those which were demanded by the dimensions of the sylphons. This led to an independent determination of the densities of the five isomers by measurement in a specific gravity bottle containing about 4 gm., the weighings being made to a fraction of a milligram. These specially determined densities are given in the following, and were used as fundamental in reducing measured changes of total volume to fractional changes of volume. As an additional check, Professor Conant was so kind as to have measured in his laboratory the index of refraction for the sodium D line at 25°, from which the molecular refraction can be calculated by combining with my densities. These values are given in the following, as well as the indices and the molecular refractions supplied me by Professor Reid, which I understand are not yet published. The theoretical value for the molecular refraction for all five isomers, disregarding structural differences, is 40.79.

Detailed Data.

Triethanolamine. This was most kindly purified under the direction of Professor J. B. Conant of the Chemistry Department by distillation in vacuum over BaO, in order to remove as much of the water as possible, which nevertheless in the opinion of Professor Conant was not completely accomplished. The product of the distillation was a liquid, clear, but of a distinct yellow color. This became browner and cloudy by the end of the filling process. The liquid is extremely viscous and two days were taken in filling the sylphon; the final touches to the filling operation were given at 95° and at 3 mm. pressure. During the filling the liquid was kept under a bell jar or other closed container with $CaCl_2$ present in order to prevent the absorption of water from the air.

Because of the extreme viscosity and unknown liability to freezing the measurements were made in an unusual order: first at 50° to 1000 kg., without return, then immediately to 95° at 1000, and at 95° to 10000 and return with good check, then to 0°, first at atmospheric pressure, and then to 1000, where there was evidence of freezing, which persisted on releasing pressure to atmospheric. The probability is that this, like glycerine, will support great subcooling under ordinary conditions. The normal melting point is given in the Eastman Catalogue as 17° to 19°. Temperature was then raised to 50° with good check in spite of the apparent freezing at 0°, and

TABLE I.

TRIETHANOLAMINE.

Pressure kg/cm²	Related Volumes		
	0°	50°	95°
0	1.0000	1.0251	
500	.9835	1.0075	
1000	.9699	.9921	1.0130
1500		.9786	.9978
2000		.9666	.9851
3000		.9464	.9637
4000		.9302	.9463
5000		.9163	.9308
6000			.9176
7000			.9057
8000			.8944
9000			.8848
10000			.8758

finally at 50° pressure was raised to 5500 and back with good check and no further evidence of freezing. Discarding one point at 50°, the average departure from smooth curves of a single one of the 37 readings was 0.13% of the maximum effect.

The relative volumes are given in Table I. The volume decrements are for 1.157 gm. The measured density at atmospheric pressure at 26.2° was 1.142, and the volume expansion of 1 gm. at atmospheric pressure between 0° and 50° was taken to be 0.0216 cm³ from direct measurement in the sylphon. This substance is not listed in I. C. T., so no comparison with previous values is attempted.

n-propyl chloride. Runs were made without incident at 0° and 50° to 12000 kg/cm², but at 95° pressure was allowed to get too low, permanently deforming the sylphon and probably developing a small leak, which, however, was not discovered until the completion of the run. A repetition was therefore attempted with a second sylphon, but this proved defective and leaked. A third sylphon was therefore used for the run at 95°; this gave a perfect check on releasing pressure, and also on returning at 95° after excursions to 0° and 50°. Connection was established with the previous runs at 0° and 50° by measurements at 1000 and 5000 at both these temperatures. The average deviation from smooth curves of a single one of the 38 points obtained at 0° and 50° with the first sylphon was 0.06% of the maximum effect; the results with the third sylphon were equally as smooth.

TABLE II.

N-PROPYL CHLORIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0757	
500	.9555	1.0046	
1000	.9261	.9645	1.0084
1500	.9024	.9357	.9734
2000	.8833	.9134	.9463
3000	.8541	.8790	.9051
4000	.8319	.8531	.8766
5000	.8138	.8324	.8539
6000	.7987	.8155	.8350
7000	.7852	.8003	.8192
8000	.7732	.7875	.8052
9000	.7625	.7759	.7929
10000	.7526	.7658	.7817
11000	.7440	.7563	.7723
12000	.7366	.7476	.7632

The numerical results are given in Table II. As explained, the relative volumes at 0° and 50° were obtained with one sylphon and those at 95° with another. The volumes obtained at 1000 and 5000 at 0° and 50° with the latter sylphon by way of check were not as good

as could be desired, and were on the average 0.0030 higher than those obtained with the first sylphon. It is probable, therefore, that the 95° results for this liquid are not as good as usual, and less weight should be attached to them.

The volumes of the table at 0° and 50° are for 0.9160 gm. The measured expansion of 1 gm at atmospheric pressure between 0° and 50° was 0.0823 cm^3, and the measured density at atmospheric pressure at 24° was 0.8839. I. C. T. gives for the density at 20° 0.890.

n-propyl bromide. Two sylphons were used for this liquid. Runs were made in the regular order at 0°, 50°, and 95°. There were irregularities at the maximum pressure at 0° with the first sylphon, which, however, seemed to have no effect on the later readings, checks being obtained between the readings with increasing and decreasing pressure. A check was not obtained, however, after the run at 95° at 0° at atmospheric pressure, and examination of the sylphon disclosed a leak. The complete series of runs was therefore repeated with a second sylphon. On working up the results, much greater irregularity was disclosed by the high pressure measurements at 0°,

TABLE III.

N-PROPYL BROMIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0655	
500	.9626	1.0114	1.0561
1000	.9356	.9750	1.0113
1500	.9146	.9491	.9780
2000	.8973	.9289	.9535
3000	.8695	.8963	.9176
4000	.8476	.8705	.8901
5000	.8291	.8499	.8673
6000	.8134	.8332	.8485
7000	.8000	.8182	.8318
8000	.7887	.8060	.8177
9000	.7784	.7943	.8052
10000	.7687	.7835	.7944
11000	.7595	.7739	.7846
12000	.7515	.7653	.7754

the irregularity being so great that the results of the first run are doubtless to be preferred. It seems now that there can be little doubt that freezing took place at the highest pressures at 0° and that both sylphons were weakened at this time, but that the actual leak in the first sylphon developed only after release of pressure to nearly atmospheric at 95°. The following table is based on the results obtained with the first sylphon. The average deviation from smooth curves of a single one of the 61 readings was 0.11% of the maximum effect.

The volumes given in Table III are for 1.3777 gm. The measured density at 25° was 1.3337, and the expansion of 1 gm between 0° and 50°, 0.0478 cm^3. I. C. T. gives for the density at 20° 1.353.

n-propyl iodide. This was prepared under the direction of Professor Conant by shaking with "hypo" and $CaCl_2$ and then fractional distillation. It was kept in the dark after purification to avoid decomposition.

TABLE IV.

N-PROPYL IODIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0509	
500	.9656	1.0085	
1000	.9412	.9775	1.0106
1500	.9214	.9528	.9813
2000	.9055	.9336	.9595
3000	.8795	.9027	.9238
4000	.8581	.8792	.8973
5000	.8409	.8594	.8755
6000	.8262	.8435	.8577
7000	.8128	.8289	.8422
8000	.8012	.8163	.8288
9000	.7906	.8049	.8169
10000	.7810	.7945	.8060
11000	.7715	.7850	.7961
12000	.7625	.7761	.7864

Measurements on this were made without incident; the conventional order was followed, 0°, 50°, 95°, and then the return check reading at 0°. The average deviation from smooth curves of a single one of the 51 readings was 0.04%.

The relative volumes are given in Table IV, which is constructed for 1.778 gm. The observed density at atmospheric pressure at 24.5° was 1.7303, and the measured expansion of 1 gm. between 0° and 50°, 0.0319 cm³. I. C. T. gives for the density at 20° 1.747.

n-butyl chloride. Runs were made on this without incident except for a leak at the gauge plug, which was repaired without displacing the sylphon. The conventional runs at 0°, 50°, 95°, and return check reading at 0° were made. At 0° the maximum pressure reached

TABLE V.

N-BUTYL CHLORIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0614	
500	.9598	1.0066	1.0526
1000	.9310	.9695	1.0062
1500	.9098	.9436	.9728
2000	.8928	.9234	.9491
3000	.8657	.8896	.9111
4000	.8438	.8651	.8835
5000	.8266	.8455	.8616
6000	.8116	.8285	.8435
7000	.7984	.8143	.8277
8000	.7867	.8011	.8133
9000	.7762	.7900	.8012
10000	.7663	.7796	.7904
11000	.7569	.7704	.7810
12000		.7618	.7727

was only 10500 instead of the usual 12000. This restriction in range was not due to freezing, but was compelled by reaching the end of the stroke of the piston because of the leak at the gauge coil. It did not seem worth while to repeat the measurements in order to remedy the deficiency. The average deviation from smooth curves of a single one of the 65 readings was 0.08% of the maximum effect.

Relative volumes are given in Table V, which is constructed for 0.9063 gm. The measured density at atmospheric pressure at 25° was 0.8796, and the measured expansion of 1 gm between 0° and 50°, 0.0675 cm³. I. C. T. gives for the density at 20° 0.884.

n-butyl bromide. The measurements on this substance went without accident or incident. The material was used without purification directly as received from Eastman. It was especially noticed on emptying the sylphon at the end of the runs that the liquid remained clear and colorless. Runs were made as usual at 0°, 50°, and 95°, to 12000 at each temperature, and then the return check reading at 0°. The average deviation from smooth curves of a single one of the 60 readings was 0.016% of the maximum effect.

TABLE VI.

N-BUTYL BROMIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0613	
500	.9641	1.0101	1.0512
1000	.9384	.9759	1.0102
1500	.9191	.9499	.9788
2000	.9025	.9297	.9554
3000	.8743	.8993	.9202
4000	.8531	.8759	.8942
5000	.8363	.8565	.8717
6000	.8214	.8392	.8530
7000	.8084	.8243	.8377
8000	.7968	.8115	.8244
9000	.7862	.8005	.8123
10000	.7767	.7902	.8014
11000	.7683	.7811	.7919
12000	.7609	.7726	.7836

Relative volumes are given in Table VI, which is constructed for 1.3063 gm. At atmospheric pressure the measured density at 25° was 1.2685, and the expansion of 1 gm between 0° and 50°, 0.0452 cm³. I. C. T. gives for the density at 20° 1.275.

n-butyl iodide. This was purified under the direction of Professor Conant in the same way as propyl iodide, and it was similarly protected from the action of light before use. The conventional runs at 0°, 50°, and 95° and the return check reading at 0° were made without incident. When the sylphon was emptied at the end of the

run a perceptible but small amount of reddish sediment was found, which doubtless was stannic iodide, from the solder of the sylphon. The iodides always seem to have some chemical activity; they are always perceptibly colored by dissociated iodine, which doubtless is the active agent. However, the amount of such activity was very slight because the return check reading at 0° after the high pressure runs was as good or better than usual. The average deviation from smooth curves of a single one of the 53 readings was 0.08% of the maximum effect.

TABLE VII.

N-BUTYL IODIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0508	
500	.9687	1.0094	1.0458
1000	.9453	.9785	1.0104
1500	.9258	.9545	.9821
2000	.9104	.9357	.9606
3000	.8841	.9069	.9249
4000	.8630	.8827	.8995
5000	.8463	.8639	.8792
6000	.8317	.8474	.8616
7000	.8183	.8331	.8462
8000	.8062	.8206	.8331
9000	.7955	.8097	.8212
10000	.7859	.7995	.8106
11000	.7765	.7905	.8007
12000	.7686	.7822	.7922

Relative volumes are shown in Table VII, which is constructed for 1.6443 gm. At atmospheric pressure the measured density at 24.5° was 1.6043, and the measured expansion of 1 gm between 0° and 50°, 0.0308 cm³. I. C. T. gives for the density at 20° 1.617.

n-amyl chloride. At 50° and 95° and at the low pressure end of the 0° run results went smoothly without incident. On the initial application of pressure at 0° it was difficult to get readings above 6000 because of high resistance at the moving contact against the slide wire, and those readings which were obtained were very much more irregu-

lar than usual. This was ascribed to an improper configuration of the flexible leads. After the first run at 0°, when a maximum of only 8000 kg was attained, the sylphon was removed from the press and the difficulty with the leads apparently remedied, as proved by the perfectly satisfactory subsequent readings at 50° and 95°. On repeating the 0° run however, after a perfect check at atmospheric pressure, there was again trouble of some sort, for the readings were again irregular, although there was no difficulty with the contact as

TABLE VIII.

N-AMYL CHLORIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0617	
500	.9632	1.0080	
1000	.9369	.9739	1.0064
1500	.9156	.9481	.9766
2000	.8982	.9277	.9526
3000	.8712	.8956	.9165
4000	.8491	.8716	.8891
5000	.8319	.8515	.8678
6000	.8180	.8350	.8498
7000	.8059	.8206	.8346
8000	.7948	.8082	.8213
9000	.7845	.7971	.8093
10000	.7748	.7866	.7987
11000	.7660	.7777	.7883
12000		.7696	.7792

before. The maximum pressure reached on the repetition at 0° was 10100. It is not unlikely that the irregularities were due to partial freezing. The average deviation from smooth curves of a single one of the 33 readings at 50° and 95° was 0.05% of the maximum effect, while at 0° the corresponding deviation for 25 readings was 0.27%. At 0° practically all of the irregularity occurred below 6000.

Relative volumes are shown in Table VIII, which is constructed for 0.9143 gm. At atmospheric pressure the measured density at 25° was 0.8872, and the measured expansion of 1 gm between 0° and 50°,

0.0670 cm³. I. C. T. gives for the density at 20° 0.883, less than my value at 25°, and indicative of a real discrepancy, although a slight one.

n-amyl bromide. This was purified under the direction of Professor Conant in the same way as the iodides. Two complete runs were made with this material with two sylphons. At 0° on the first run pressure was pushed to 11700, which apparently froze the liquid. After the termination of the 50° and the 95° runs the sylphon was

TABLE IX.

N-AMYL BROMIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0573	
500	.9680	1.0090	
1000	.9428	.9770	1.0101
1500	.9233	.9528	.9803
2000	.9072	.9338	.9588
3000	.8807	.9031	.9241
4000	.8600	.8795	.8975
5000	.8429	.8599	.8766
6000	.8284	.8439	.8590
7000	.8153	.8299	.8438
8000	.8036	.8172	.8301
9000	.7930	.8063	.8182
10000		.7971	.8081
11000		.7879	.7990
12000		.7790	.7905

found to have lost considerable weight, leak evidently having been produced by damage during freezing. The readings were therefore discarded, and the runs repeated with another sylphon. There was no special incident during the runs with the second sylphon, except that on the initial application of pressure up to about 5000 at 0° a leak developed in the connecting pipe which made it necessary to release the pressure to zero, renew the washers on the pipe, and repeat the run. The maximum pressure at 0° was now restricted to 9000, at which there was no trace of any freezing phenomenon. Runs were

made at 50° and 95° to the full 12000 and return without incident, and then the return check reading was made at 0°. The check was not as good as usual, so that it seemed desirable to repeat the entire 0° run. This was done with a satisfactory check at all the points except atmospheric pressure. On taking down the apparatus, weighing the sylphon indicated no trace of leak. No certain explanation could be found for the unusually large discrepancies at 0° at atmospheric pressure; it is possible that unusually high friction in the internal guides of the sylphon may have been responsible. However, in view of the checks at all other pressures, there is no reason to fear important error. The volume assumed at 0° at atmospheric pressure was the mean of the two volumes on the first application, which differed by only 0.1% from the mean. The mean of the two zeroes on the second application also agreed with the first mean. The mean deviation from smooth curves of a single one of the 50 readings (discarding the atmospheric readings at 0°) was 0.07%.

Relative volumes are given in Table IX, which is constructed for 1.2505 gm. At atmospheric pressure the measured density at 24.5° was 1.2616; I. C. T. gives 1.223 at 20°. The expansion of 1 gm at atmospheric pressure between 0° and 50° was not obtained by direct measurement, but at 50° an extrapolation to atmospheric pressure was made from 100 kg; the range of extrapolation is so slight that there can be no important error. The value thus found for the expansion was 0.0456 cm^3.

n-amyl iodide. This was purified under the direction of Professor Conant in the same way as the other iodides and butyl bromide. The sylphon was filled in a darkened room to avoid decomposition. Regular runs were made without incident at 0° and 50°. At 0° the full 12000 was applied with no signs of freezing, although when the results were plotted on a large scale the irregularities beyond 9000 at 0° seemed somewhat larger than usual. One would have been prepared for freezing in view of the known freezing of amyl chloride and bromide; it may well be that the liquid subcooled and the irregularity of the high pressure points at 0° may have been due to the great viscosity of the subcooled liquid. On completing the run at 50° and passing to 95°, a short circuit developed in the leads which made it necessary to take the apparatus apart, without, however, touching the sylphon. The apparatus was then reassembled, and the 95° run, up and down, made with satisfactory results, but on trying for the lowest reading at 95° trouble of some sort again developed in the connections, making the reading impossible. Neither was it possible

to get readings at 50° and 0°, so that the usual check could not be made. On hunting for the trouble after dismounting the apparatus the sylphon was found to have developed a leak, with a total loss of weight of 0.2 gm. It was therefore necessary to repeat the measurements with a new sylphon, but in view of the regularity of the readings with the first sylphon up to the very end, the simple check was first made of determining the difference between the 0°, 50°, and 95° isotherms at atmospheric and 5000 kg/cm² with the new sylphon.

TABLE X.

N-AMYL IODIDE.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0529	
500	.9685	1.0100	
1000	.9442	.9793	1.0093
1500	.9250	.9559	.9806
2000	.9094	.9376	.9585
3000	.8831	.9080	.9247
4000	.8624	.8835	.8994
5000	.8451	.8640	.8783
6000	.8304	.8476	.8607
7000	.8173	.8337	.8453
8000	.8064	.8211	.8312
9000	.7965	.8105	.8192
10000	.7873	.8006	.8085
11000	.7786	.7911	.7987
12000	.7706	.7816	.7896

These were found to check perfectly, so that further repetition was dispensed with. It is evident that the leak in the first sylphon must have developed after the last reading at 95°.

The average deviation from smooth curves of a single one of the 55 readings with the first sylphon was 0.10% of the maximum effect.

Relative volumes are given in Table X, which is constructed for 1.5683 gm. The measured density at atmospheric pressure at 24.5° was 1.5287; I. C. T. gives 1.517 at 20°, less than my value at 24.5°, indicating some discrepancy. It would seem probable that any

ordinary impurity would make the liquid lighter rather than heavier. The atmospheric volume at 50° was obtained, as for the preceding liquid, by an extrapolation from 100 kg. The expansion of 1 gm between 0° and 50° was found to be 0.0331 cm³.

Octanol-3. $C-C-C(CH_3)-C-C-C-C-C$. The initial attempt to get a run at 95° failed because of a ground on one of the connections. This was repaired without disturbing the sylphon, and

TABLE XI.

OCTANOL-3

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0480	
500	.9697	1.0090	
1000	.9479	.9800	1.0105
1500	.9301	.9583	.9849
2000	.9156	.9407	.9646
3000	.8916	.9124	.9332
4000	.8722	.8910	.9086
5000		.8737	.8891
6000		.8584	.8728
7000		.8452	.8589
8000		.8338	.8465
9000			.8349
10000			.8250
11000			.8158
12000			.8073

three successful runs obtained in the order 50°, 0°, 95°. The final points at 95° agreed with the initial ones before the short circuit developed, so that the usual check at 0° was not necessary. The average deviation from smooth curves of a single one of the 48 readings was 0.10% of the maximum effect.

Relative volumes are given in Table XI, which is constructed for 0.8370 gm. At atmospheric pressure the measured density at 22.2° was 0.8177, and the thermal expansion of 1 gm between 0° and 50°

0.0574 cm³. Professor Conant's index of refraction was 1.4251, which combined with my density gives 40.74 for the refraction constant. Professor Reid's values for index and refraction constant are 1.4209 and 40.41 respectively. All these are at 25°.

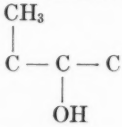
2-methyl heptanol-3.  Runs were

TABLE XII.

2-METHYL HEPTANOL-3.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0505	
500	.9690	1.0078	
1000	.9459	.9789	1.0121
1500	.9283	.9565	.9851
2000	.9140	.9394	.9647
3000	.8897	.9216	.9428
4000	.8707	.8891	.9080
5000	.8544	.8714	.8888
6000		.8568	.8719
7000		.8435	.8569
8000		.8318	.8441
9000		.8213	.8331
10000		.8117	.8232
11000			.8139
12000			.8049

made without incident at 50°, 0°, 95°, and the return check reading at 50°. The average deviation from smooth curves of a single one of the 51 readings was 0.08% of the maximum effect.

Relative volumes are given in Table XII, which is constructed for 0.8392 gm. At atmospheric pressure the measured density at 22.2° was 0.8211, and the thermal expansion of 1 gm between 0° and 50°, 0.0603 cm³. Professor Conant's index of refraction was 1.4255, which combined with my density gives 40.68 for the refraction con-

stant. Professor Reid's values for index and refraction constant are 1.4246 and 40.31 respectively, all for 25°.

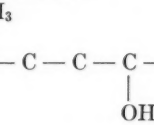
2-methyl heptanol-5.  Runs were

TABLE XIII.

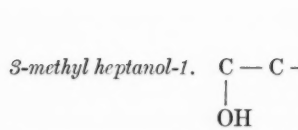
2-METHYL HEPTANOL-5

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0477	
500	.9679	1.0071	
1000	.9449	.9774	1.0085
1500	.9269	.9549	.9815
2000	.9122	.9375	.9612
3000	.8882	.9099	.9297
4000	.8698	.8887	.9054
5000	.8538	.8716	.8855
6000		.8561	.8696
7000		.8425	.8556
8000		.8305	.8433
9000		.8198	.8318
10000		.8102	.8220
11000		.8023	.8127
12000			.8038

made without incident at 50°, 0°, 95°, and the return check reading at 50°. The average deviation from smooth curves of a single one of the 49 readings was 0.05%.

Relative volumes are given in Table XIII, which is constructed for 0.8337 gm. At atmospheric pressure the measured density at 24.4° was 0.8147, and the thermal expansion of 1 gm between 0° and 50°, 0.0571 cm³. Unfortunately there was not enough of the material to permit a measurement of its index. Professor Reid's value for index and refraction constant are 1.4112 and 41.65 respectively.

3-methyl heptanol-1.



Compressibility measurements were made without incident at 50°, 0°, 95°, and the return check reading at 50°. The average deviation from smooth curves of a single one of the 50 readings was 0.03%.

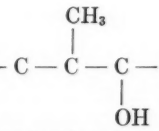
TABLE XIV.

3-METHYL HEPTANOL-1.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0446	
500	.9714	1.0065	
1000	.9499	.9791	1.0090
1500	.9323	.9585	.9834
2000	.9181	.9422	.9642
3000	.8946	.9147	.9342
4000	.8760	.8939	.9105
5000	.8605	.8764	.8912
6000	.8468	.8616	.8748
7000	.8341	.8482	.8611
8000		.8366	.8487
9000		.8260	.8371
10000		.8167	.8270
11000		.8083	.8179
12000			.8098

Relative volumes are given in Table XIV, which is constructed for 0.8426 gm. The density measured at atmospheric pressure at 22.2° is 0.8265, and the expansion of 1 gm between 0° and 50°, 0.0530. Professor Conant's index of refraction was 1.4304, which combined with my density gives for the refraction constant 40.82. Professor Reid's values for index and refraction constant are respectively 1.4225 and 42.21.

3-methyl heptanol-4.



Compressibility runs were made without incident at 50°, 95°, 0°, and the return check reading at 50°. The average deviation from smooth curves of a single one of the 54 readings was 0.09%.

TABLE XV.

3-METHYL HEPTANOL-4.

Pressure kg/cm²	Relative Volumes		
	0°	50°	95°
0	1.0000	1.0506	
500	.9697	1.0091	
1000	.9476	.9814	1.0125
1500	.9305	.9599	.9864
2000	.9162	.9421	.9664
3000	.8929	.9146	.9349
4000	.8739	.8925	.9101
5000	.8591	.8762	.8917
6000	.8453	.8614	.8754
7000		.8490	.8614
8000		.8368	.8487
9000		.8263	.8381
10000		.8167	.8283
11000		.8081	.8193
12000			.8109

Relative volumes are shown in Table XV, which is constructed for 0.8455 gm. The density measured at atmospheric pressure at 22.2° is 0.8272, and the expansion of 1 gm between 0° and 50°, 0.0599. Professor Conant's index of refraction was 1.4286, which combined with my density gives for the refraction constant 40.92. Professor Reid's values for index and refraction constant are respectively 1.4211 and 39.61.

Discussion.

This discussion will not be concerned with general features of the pressure-volume-temperature relations which are common to all liquids, for these have been sufficiently considered in previous papers, but we shall be interested only in features characteristic of these particular liquids.

Triethanolamine ($N(C_2H_5O)_3$) was tried, as already stated, because experience with glycerine and similar compounds had suggested that the three OH groups might give it unusual incompressibility. As a matter of fact the compressibility is about 50 per cent greater than that of glycerine, which thus retains its position as the most incompressible organic compound, and is almost exactly the same as that of ethylene glycol. It is to be considered, however, that the rest of the molecule of triethanolamine is much more complicated than in the case of either glycerine or ethylene glycol, so that the OH groups occupy a proportionally smaller part of the total structure. The fact that the compressibility is so low in spite of the greater complication of the rest of the molecule is again evidence of the great effect of the OH group in consolidating the entire molecular structure and imparting to it relative incompressibility.

Consider next the halogen compounds. The most outstanding effect of the addition of a halogen is that the substance is carried away from the gaseous condition toward incompressibility and liquidity. Propane and butane are, of course, under ordinary conditions gaseous, while pentane is one of the most compressible of liquids. The addition of the halogen lowers the vapor pressure and decreases the compressibility by a marked degree. At 0° the volume compression under 10000 kg/cm^2 of the amyl halogens is roughly about 0.8 as much as that of normal pentane. The compression of amyl alcohol is about the same as that of the halogen compounds, so that roughly the effect of a halogen is about the same as that of an OH group in decreasing the compressibility.

If the relative volumes at 50° of the nine halogen compounds are plotted against pressure in the same diagram, certain regularities stand out. In the groups containing a common halogen the compressibility decreases on passing from propyl to butyl to amyl groups, that is, in the direction of increasing molecular weight, and in the groups containing a common alkyl the compressibility decreases as the atomic weight of the halogen increases. An exception to this general trend are butyl and amyl iodides, which have almost exactly the same compressibility.

If the volume increment on increasing temperature at constant pressure is plotted against pressure, curves will be obtained which drop rapidly with increasing pressure, as has been universally found before. The decrease of thermal expansion with increasing pressure is, however, not so large as has been previously found for other classes of compounds. As a rough average the thermal expansion of these alkyl halides at 12000 kg/cm^2 is between one third and one fourth of its value at atmospheric pressure. Among other substances instances are not uncommon in which the drop is twice as rapid. In smaller detail, the curves of thermal expansion against pressure are not entirely smooth, but exhibit various episodes, as has been previously found for other liquids. Among the most striking of such episodes shown by the alkyl halides is a stretch from 2000 to 6000 kg for butyl bromide, for which the thermal expansion between 0° and 50° is higher than is to be expected from the rest of the curve, and the last 6000 kg of the curve for butyl iodide, which shows a nearly constant expansion between 0° and 50°.

Without doubt the most significant method of analysis for the nine alkyl halides is to compare the molecular volumes instead of the relative volumes as given in the tables. The molecular volumes are obtained at once from the data of the tables by dividing the figures there given by the number of grams for which the tables are constructed (that is, by the density at 0° C at atmospheric pressure), and multiplying by the molecular weight. The volumes thus obtained may be compared either by comparing the volume increments on changing the alkyl group, keeping the halogen fixed, or by changing the halogen, keeping the alkyl group fixed. The differences of molecular volume obtained in this way are given in Tables XVI and XVII.

Table XVI gives the increments of volume on adding a CH_2 group to the molecule. It is in the first place evident that this volume is a strong function of pressure, that is, the additional space required on forcing a CH_2 group into the molecule becomes less as pressure increases. This is naturally to be described as due to the compression of the CH_2 group itself. The absolute value of the volume of the CH_2 group varies considerably, depending on the kind of molecule to which it is attached, as may be seen by an inspection of the table, the range being from 17.09 to 15.36 at atmospheric pressure, and from 13.69 to 11.18 at 12000. The proportional loss of volume with pressure, as shown by the decrement in any of the columns of Table XVI, is more nearly constant. Disregarding the initial entry in the first column, which is abnormal and is connected with the abnormally

large volume of propyl chloride due to the nearness of the critical point, the volume of the CH_2 group at 12000 varies from 0.72 to 0.79 of its volume at atmospheric pressure. The ratio of the total volume of the compound at 12000 to that at atmospheric pressure varies from 0.72 to 0.75. The average compressibility of the CH_2 is therefore approximately the same as that of the entire compound, not a particularly surprising result.

The increment of volume on adding a CH_2 group to propyl chloride or iodide to form the butyl compound is less than the increment on

TABLE XVI.

DIFFERENCES OF MOLECULAR VOLUMES AT 50°.

Pressure kg/cm²	Propyl chloride to butyl chloride	Butyl chloride to amyl chloride	Propyl bromide to butyl bromide	Butyl bromide to amyl bromide	Propyl iodide to butyl iodide	Butyl iodide to amyl iodide
0	16.15	15.36	16.28	16.37	17.09	15.38
500	16.63	14.75	15.62	15.92	16.53	14.57
1000	16.29	14.56	15.31	15.62	16.01	14.18
1500	16.13	14.13	14.91	15.42	15.68	13.96
2000	15.98	13.85	14.57	15.27	15.47	13.67
3000	15.46	13.55	14.32	14.73	15.13	13.20
4000	15.20	13.25	14.16	14.35	14.70	12.78
5000	14.98	12.85	13.98	14.01	14.48	12.45
6000	14.67	12.72	13.65	13.85	14.17	12.21
7000	14.53	12.49	13.41	13.74	13.97	12.05
8000	14.28	12.40	13.17	13.57	13.76	11.86
9000	14.14	12.27	13.06	13.39	13.64	11.76
10000	13.94	12.08	12.92	13.40	13.48	11.62
11000	13.82	11.98	12.87	13.19	13.37	11.46
12000	13.69	11.91	12.70	13.04	13.30	11.18

adding CH_2 to butyl chloride or iodide to form amyl chloride or iodide. This means that as the molecule becomes more complex the increment of volume due to the addition of successive CH_2 groups becomes less, as seems not unnatural. This sequence does not hold for the bromides, however. Examination shows that the sequence would be restored if the volumes of butyl bromide were increased somewhat. Table XVII, as will be shown in more detail presently, indicates the

same sort of thing, namely that butyl bromide has at all pressures a volume somewhat too small to fit in regularly with that of the other compounds.

Consider next Table XVII, which shows the differences of volume between chlorine and bromine and between bromine and iodine in the various compounds. The state of affairs is entirely different from that of Table XVI; here the columns at first increase with in-

TABLE XVII.

DIFFERENCES OF MOLECULAR VOLUMES AT 50°.

Pressure kg/cm²	Propyl chloride to propyl bromide	Propyl bromide to propyl iodide	Butyl chloride to butyl bromide	Butyl bromide to butyl iodide	Amyl chloride to amyl bromide	Amyl bromide to amyl iodide
0	2.80	5.46	2.93	6.27	3.94	5.28
500	4.19	6.11	3.18	7.02	4.35	5.67
1000	4.36	6.42	3.38	7.12	4.44	5.68
1500	4.51	6.37	3.29	7.14	4.48	5.68
2000	4.63	6.30	3.32	7.20	4.64	5.60
3000	4.64	6.32	3.50	7.13	4.68	5.60
4000	4.56	6.38	3.52	6.92	4.62	5.35
5000	4.50	6.31	3.50	6.81	4.66	5.25
6000	4.45	6.28	3.53	6.80	4.56	5.16
7000	4.44	6.20	3.32	6.76	4.57	5.07
8000	4.43	6.11	3.32	6.70	4.49	4.99
9000	4.40	6.04	3.32	6.62	4.44	4.99
10000	4.31	6.02	3.29	6.58	4.61	4.80
11000	4.24	6.01	3.29	6.51	4.50	4.78
12000	4.23	5.90	3.24	6.50	4.37	4.64

creasing pressure and then fall off somewhat. The total range of variation is less than in Table XVI. A possible explanation is obviously that the volumes of chlorine, bromine, and iodine are not the same sort of functions of pressure, but the compressibility of chlorine varies rapidly with pressure, dropping off rapidly with increasing pressure at the low pressure end of the range, the compressibility of bromine is intermediate in behavior, while the compressibility of iodine remains more nearly constant over the entire pressure range. A simple graphical construction will show at once the plausibility of

such an explanation, which is, moreover, consistent with what other lines of evidence would lead us to expect.

In all cases the difference of volume betweeen bromine and chlorine is less than the difference between iodine and bromine. This difference is much accentuated in the butyl compounds. The butyl compounds would fall more nearly into line with the others if the volumes of butyl bromide were somewhat increased, showing, as already suggested, that the volume of butyl bromide is anomalously low.

TABLE XVIII.

VOLUMES AT 50° OF 0.8392 GRAMS OF VARIOUS OCTANOLS.

Pressure kg/cm²	Octanol-3	2-methyl heptanol-3	2-methyl heptanol-5	3-methyl heptanol-1	3-methyl heptanol-4
0	1.0508	1.0505	1.0546	1.0404	1.0428
500	1.0116	1.0078	1.0137	1.0024	1.0016
1000	.9826	.9789	.9838	.9752	.9741
1500	.9608	.9565	.9612	.9546	.9527
2000	.9432	.9394	.9437	.9384	.9351
3000	.9148	.9216	.9159	.9110	.9078
4000	.8933	.8891	.8946	.8903	.8858
5000	.8760	.8714	.8773	.8729	.8697
6000	.8606	.8568	.8618	.8581	.8550
7000	.8474	.8435	.8481	.8448	.8427
8000	.8360	.8318	.8360	.8322	.8306
9000		.8213	.8252	.8227	.8201
10000		.8117	.8156	.8134	.8106
11000			.8076	.8050	.8021

The difference between the volumes of the halogens in these compounds is several fold greater than one would calculate from the atomic radii in solid compounds as given by X-ray analysis.

Finally, consider the volumes of the isomers of octyl alcohol. The comparison here should be of the volumes of equal masses. In Table XVIII are shown the volumes at 50° in cm^3 of 0.8392 gm, 0.8392 being very nearly the average density of the five isomers at 0°. The most striking feature is doubtless the approximate equality of the volumes of all five isomers at all pressures. The range of variation becomes less as pressure increases, the extreme

variation at the maximum pressure being somewhat less than half of the variation at atmospheric pressure, but the effect is not striking because the variation is everywhere so small. Furthermore, the volume of every *pair* of substances does not tend to become more nearly equal at high pressure, as can be seen at once from the table in the case of octanol-3 and 2-methyl heptanol-3. 2-methyl heptanol-1 and 3-methyl heptanol-4 are a pair whose volume curves cross. Further study of the details of Table XVIII does not appear profitable at present. It was a considerable disappointment to find the situation so featureless. This, in addition to previous experience, has convinced me that the behavior of isomers under high pressure is so similar that it will not pay to examine the question experimentally further until there is some theory which will indicate just what the crucial effects may be.

One would expect that the average compressibility of the octanols would be less than that of octane, according to the general rule that the addition of an OH group decreases the compressibility. This is in fact the case; for example, the compression of n-octane at 50° under a pressure of 7000 kg/cm^2 (the highest pressure at which n-octane is liquid at that temperature) is 1.16 times as great as the compression of octanol-3 under the same conditions.

I am indebted to my assistant Mr. L. H. Abbot for making the readings. I am also indebted for financial assistance to the Rumford Fund of the American Academy of Arts and Sciences for the purchase of supplies, and to the Milton Fund of Harvard University for the salary of my assistant.

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REFERENCES.

[1] P. W. Bridgman, Proc. Amer. Acad. 66, 185–233, 1931; 67, 1–27, 1932.

[2] P. W. Bridgman, Proc. Amer. Acad. 47, 347–438, 1912; 47, 441–558, 1912; 51, 55–124, 1915; 52, 91–187, 1916. Phys. Rev. 3, 126–141, 153–203, 1914; 6, 1–33, 94–112, 1915.